

Elemental Analysis of Glass by Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES)

1 Scope

1.1 Introduction

The concentrations of selected elements in glass serve to chemically characterize the source of the glass. The concentrations of several elements are intentionally controlled by the manufacturers to impart specific end-use properties to a particular glass product. These manufacturer-controlled elements help to chemically characterize a glass fragment by placing it into a particular product use class. The concentrations of trace elements are generally not controlled by the manufacturers. Subtle and distinct differences in the concentrations of manufacturer-controlled elements and uncontrolled trace elements provide a means of differentiating among glasses made by different manufacturers, among glasses from different product lines of a single manufacturer, and over time along an individual production line of glass from a single manufacturer.

1.2 Principle

This procedure applies to Geologist-Forensic Examiners who determine the concentrations of aluminum (Al), barium (Ba), calcium (Ca), iron (Fe), magnesium (Mg), manganese (Mn), sodium (Na), strontium (Sr), titanium (Ti), and zirconium (Zr) in glass fragments in the Trace Evidence Unit (TEU) using of inductively coupled plasma-optical emission spectrometry (ICP-OES). The analysis is performed by dissolving the glass and using the method of ICP-OES for analytical measurements. Quantitative determination of individual element concentrations is achieved by comparing specimens with solutions of matrix matched standards. The procedure can be adapted for the determination of concentrations of additional elements when needed. Refer to Koons et al. (1988) for further information about ICP-OES.

1.3 Specimens

This procedure is used for the analysis of small fragments of broken glass objects such as: windows, windshields, or containers. When possible, triplicate sub-samples, each weighing 5-8 mg, are selected for analysis from each glass item of interest for dilution to 10 ml of solution. If only 5 ml of the final dilution is to be made, samples as small as 2 mg may be used for each sub-sample. Additional sub-samples may be analyzed at the discretion of the Geologist-Forensic Examiner.

2 Equipment/Materials/Reagents

- 1000 µg/ml Scandium Spectrometric Standard Solution (National Institute for Standards and Testing (NIST) (traceable)

- 15-ml disposable polypropylene screw top centrifuge tubes
- 5% hydrochloric acid (HCl) (Optima Grade, equivalent, or higher)
- 49% hydrofluoric acid (HF) (Optima Grade, equivalent, or higher)
- 50-ml disposable polypropylene screw top centrifuge tubes
- Analytical balance (capable of weighing objects between 1 μ g and 5000 mg, with \pm 1 μ g reproducibility, or higher)
- Pipettes or pipette tips and pipetting devices (non-glass, capable of delivering 25 μ L - 10 ml)
- Cleaning solution (e.g., Cavicide, Windex)
- Compressed air
- Concentrated hydrochloric acid (HCl) (Optima Grade, equivalent, or higher)
- Concentrated nitric acid (HNO₃) (Optima Grade, equivalent, or higher)
- Container Glass Reference Material (NIST standard reference material (SRM) 621)
- Convection oven
- Deionized water (18.2 megaohm-cm or higher)
- Erlenmeyer flask
- Ethanol (American Chemical Society (ACS) Reagent Grade, equivalent, or higher)
- Standard Glass Reference Materials (NIST SRM 1831, Schott FGS1 and FGS2)
- Glass Blank, described below, prepared by High Purity Standards or equivalent
- Jeweler's hammer, or steel mortar and pestle, or equivalent
- Kimwipes, Techwipes, or equivalent low lint paper tissue
- Laboratory balance (capable of measuring objects between 1 mg and 100 g with \pm 0.1 mg reproducibility, or higher)
- Laboratory coat
- Multi-element glass standard solution, described below as Std #1, produced by High Purity Standards, or equivalent (calibration standard)
- Multi-element glass standard solution, described below as Std #2, produced by High Purity Standards, or equivalent (calibration standard)
- Multi-element glass standard solution, described below as Std #3, produced by High Purity Standards, or equivalent (calibration standard)
- Multi-element glass standard solution, described below as Std #4, produced by High Purity Standards, or equivalent (calibration standard)
- Multi-element glass standard solution, described below as Std #5, produced by High Purity Standards, or equivalent (calibration standard)
- Nitrile gloves or equivalent
- Plastic sheets or sleeves
- Safety goggles
- Soft bristle brush
- Sonicator

- Thermo Fischer Scientific iCAP 6500 Duo ICP-OES or equivalent with an accompanying personal computer containing the instrument software (e.g., iTEVA), and a printer
- Thermometer
- Tweezers
- Vortex mixer

3 Standards and Controls

3.1 A series of five commercially available multi-element standard solutions and a calibration blank are used to produce calibration curves for every analysis. If the correlation coefficient of the calibration curve (r) for any element is less than 0.99, the analysis must be stopped and appropriate remediation measures taken prior to the resumption of the analysis. Appropriate measures could include cleaning the system, changing the tubing, changing the purge solution, checking the system alignment, or other actions as needed.

3.1.1 The solutions are prepared in a matrix composed of 5% concentrated HCl in deionized water, with 5 $\mu\text{g/ml}$ scandium as an internal standard. Table 1 shows the concentrations of the solutions used to construct the calibration curve. The solutions have a shelf-life of six months to one year. They are stored in tightly sealed containers at room temperature and pressure to maintain stability.

Table 1: Elemental Concentrations of the Standard Solutions ($\mu\text{g/ml}$, $\pm 0.5\%$)

Element	Blank	Std #1	Std #2	Std #3	Std #4	Std #5
Al	0	0.05	0.1	1	10	20
Ba	0	0.01	0.05	0.1	1	2
Ca	0	15	30	45	60	75
Fe	0	0.1	0.5	1	5	10
Mg	0	0.1	0.2	2	10	20
Mn	0	0.01	0.05	0.1	1	2
Na	0	40	60	80	100	120
Sr	0	0.01	0.05	0.1	1	2
Ti	0	0.01	0.05	0.1	1	3
Zr	0	0.01	0.05	0.1	0.5	1
Sc	5	5	5	5	5	5

3.1.2 The quality of new blank and calibration standard solutions must be verified prior to use. This verification consists of analyzing the new solutions on the ICP-OES after calibration with the prior set of blank and calibrations standards. If the concentrations of the new solutions deviate by more than 10% of their expected value, the standards will not be used.

3.1.3 Negative controls must be analyzed with every analysis. The calibration blank represents a negative control sample. If this specimen produces emission intensities equal to half the emission intensities of Standard #1, the analysis must be stopped and appropriate measures taken prior to the resumption of the analysis. Appropriate measures could include cleaning the

system, changing the tubing, changing the purge solution, checking the system alignment, preparing new solutions, or other actions as needed.

3.2 Standard glasses of known chemical composition, such as NIST SRM 1831, NIST SRM 621, FGS 1, and FGS 2 are stored at ambient temperature and pressure in separate closed containers in the glass preparation area to prevent deleterious change. Glass standards maintained in this fashion have an indefinite shelf-life.

3.2.1 Each analytical set is analyzed with appropriate standard glass samples which are used as positive control samples for that analytical run. The positive control's response will be assessed against the certified and published values for a particular control and the average values from the validation.

3.2.1.1 Triplicate samples of one or more glass standards, such as SRM 621, SRM 1831, FGS 1, FGS 2, or others appropriate for the evidence glass type, are analyzed with each case in the same manner as evidentiary samples to check the analytical precision and accuracy of the computed results.

3.2.1.2 Each standard glass measured will be assessed against the control charts for the method determined from the validation. Mean concentration values have been established for each of the glass standards using 15 samples, analyzed over five days. From these analyses, a standard deviation has been established in Table 2. A control is acceptable if the calculated mean value is within three standard deviations ($\pm 3SD$) of the control chart mean and the relative standard deviations (RSDs) are less than 10%.

Table 2: Control Chart Values

Element	Mean Measured Concentration, %				Standard Deviation			
	SRM 1831	SRM 621	FGS 1	FGS 2	SRM 1831	SRM 621	FGS 1	FGS 2
Al	0.62625	1.47257	0.14872	0.68863	0.03049	0.07839	0.00554	0.06389
Ba	0.00339	0.09280	0.00450	0.01991	0.00020	0.00497	0.00018	0.00186
Ca	6.01236	7.77289	6.22194	5.76230	0.27961	0.41200	0.21241	0.54098
Fe	0.06152	0.03116	0.05771	0.26568	0.00344	0.00822	0.00215	0.02496
Mg	2.17507	0.16749	2.44195	2.26301	0.10913	0.00856	0.08850	0.20336
Mn	0.00134	0.00184	0.00465	0.02158	0.00010	0.00012	0.00019	0.00200
Na	10.0890	9.47519	10.2725	9.51088	0.48881	0.51055	0.37675	0.90502
Sr	0.00937	0.01057	0.00602	0.02570	0.00048	0.00054	0.00021	0.00247
Ti	0.01127	0.00778	0.00702	0.03169	0.00055	0.00044	0.00030	0.00303
Zr	0.00482	0.00702	0.00530	0.02447	0.00046	0.00050	0.00033	0.00219

3.2.1.3 When precision (measured as RSD) among the standard glass replicate measurements is >10% for elements present at readily measurable levels, appropriate measures are taken to determine the cause of the discrepancy. When the measured concentrations of several elements in a standard glass have relative standard deviations >10%, the digest solutions will be reanalyzed. Digestion of additional standard glass samples may be necessary.

3.3 Each analytical set is analyzed with a digestion blank which is used as a negative control sample for that analytical run. Triplicate blank samples will be prepared with each sample set (See Section 5.1.6). The negative control's response will be assessed. Values greater than half the intensity of Calibration Standard #1 are indicative of contamination during sample preparation or pipetting errors. Data for an analytical run with high digestion blank values may still be used for comparison purposes, but only for data gathered within that analytical run.

3.4 The calibration of the analytical balances and pipettes is verified with every use and the values are recorded for each case. The calibration of the laboratory balance is checked by using 5 mg and 10 mg weights. The calibration of the pipettes is checked by weighing an appropriate volume of deionized water delivered by the pipette on a laboratory balance before use. The results are recorded. If the value measured differs from the stated value by >10%, the balance or pipette must not be used.

3.5 The quality of new hydrofluoric acid, hydrochloric acid, and scandium internal standards must be checked prior to use. Prepare and run a set of three digestion blank samples by following the instructions at 5.1.6 through 5.1.19, although it is not necessary to analyze standards, samples, or additional blanks. Values greater than half the intensity of Calibration Standard #1 are indicative of contamination in the new reagents. If high values are present, the reagents must be re-prepped and analyzed to confirm the result. Reagents returning high values after at least two checks must not be used.

4 Sampling or Sample Selection

4.1 If possible, several samples should be selected from each item to represent the range of potential compositions of the glass. When sufficient glass is available, at least three duplicate specimens will be chosen per source.

4.2 Surface fragments should be avoided if possible because of the potential for contamination from surface coatings or layers with a different composition than the bulk glass (e.g., tin on the float surface).

4.3 Five to eight milligrams of glass per replicate is considered ideal when producing 10 ml of solution. Two to five milligrams of glass may be used when more glass is unavailable, but these samples must not be diluted to more than 5 ml solution volume.

5 Procedures

5.1 Sample Preparation and Analysis

5.1.1 Prior to preparing any samples, thoroughly clean the laboratory bench surfaces and all tools/equipment to be used with a cleaning solution and wipe with a low lint material to minimize the potential for contamination.

5.1.2 Wash each glass item separately by soaking fragments for 30 minutes in concentrated HNO_3 . Rinse three times with deionized water and three times with ethanol. Dry in an oven set to 80°C . Prepare triplicate samples of the appropriate standard glass samples in the same manner. After the samples have been cleaned, handle the fragments using tweezers, gloved hands, or other clean tools.

5.1.3 Run the internal calibration routine on the analytical balance before use. Save the printout of the results in the case records. To check the calibration and to demonstrate a lack of drift in the balance during use, weigh and record the weights of 5 and/or 10 mg weights at the beginning and end of the weighing session. Drift greater than 0.01 mg may indicate a problem with the reproducibility of the balance and will necessitate re-weighing the samples.

5.1.4 Break the glass samples as necessary. To further break the glass, contain a glass fragment by placing it in the cavity of a clean, steel mortar and pestle set. Use the pestle to break the fragment. The crushed glass will be contained in the cavity by the removable metal sleeve. Carefully clean the set using a soft bristle brush and compressed air between each use. Alternately, place the fragment between two sheets of clean, thick plastic and rap the glass sharply with a jeweler's hammer (or equivalent) to crush it. Carefully remove the broken fragments from between the plastic with tweezers. Place the plastic in the glass trash receptacle. Refer to Section 9 for safety guidelines prior to breaking glass.

5.1.5 Weigh each sample to the nearest 0.01 mg and print out the results. Place each glass sample weighed in individual 15-ml centrifuge tubes. For items where there is sufficient glass to prepare triplicate sub-samples, the first sub-sample measured is identified by the sample identifier followed by the letter "a". Similarly, subsequent sub-samples are identified by the sample identifier followed by the next letter ("b," then "c," ...).

5.1.6 Add 500 μl of 49% HF to each sample and standard glass control sample tube, and to each of three empty 15-ml centrifuge tubes, which will serve as digestion blanks. Refer to Section 10 for safety guidelines prior to the use of HF.

5.1.7 Place the uncapped tubes in an oven set to 80°C . Remove the tubes from the oven after 2 hours. Sonicate the sample tubes briefly and return them to the oven until dry (typically 24 to 36 hours).

5.1.8 Remove the tubes from the oven and let them cool. To produce 10 ml of solution, carefully add 500 μl of concentrated HCl, 9.45 ml of deionized water, and 50.0 μl of scandium

internal standard solution to each tube. To produce 5 ml of solution, carefully add 250 μ l of concentrated HCl, 4.725 ml of deionized water, and 25.0 μ l of scandium internal standard solution to each tube in that order. 10 ml of solution will be produced when the glass fragment weighed \geq 5 mg prior to dissolution. 5 ml of solution will be prepared when the glass fragment weighed $<$ 5 mg prior to dissolution. Check the calibration of the pipette(s) by weighing an appropriate volume of deionized water delivered by the pipette on a laboratory balance before use.

5.1.9 Tightly cap the tubes and vortex the contents of each tube for 15 to 20 seconds. Return the tubes to the 80°C oven for one hour.

5.1.10 Remove the tubes from the oven and briefly vortex their contents. Allow the samples to stand for at least 8 hours to ensure complete dissolution.

5.1.11 Enter the sample weights, volumes, and location in the autosampler into the iTeva Analyst software used to control the instrument.

5.1.12 Vortex the sample tubes to mix the contents.

5.1.13 Place the sample tubes into the autosampler of the ICP-OES for analysis. The calibration standards are analyzed first, then the standard glass samples are analyzed, the dilution blank is analyzed next, and finally the case specimens are analyzed. Samples can be randomized (e.g., 2c followed by 3a followed by 1b, etc.) or analyzed sequentially (e.g., all “a” subsamples, followed by all “b” subsamples, etc.).

5.1.14 Use a solution of 5% HCl as the purge solution.

5.1.15 New calibration curves may be generated in the course of a sample analyses at the discretion of the Geologist/Forensic Examiner.

5.1.16 Clean the torch assembly and replace the tubing on the pump and autosampler as needed. See the instrument manual for further guidance. The tubing may be replaced and the torch cleaned more frequently at the discretion of the Geologist-Forensic Examiner.

5.1.17 Start the ICP-OES following the guidance in the instrument manual.

5.1.17.1 Turn on radio frequency (RF) generator and plug in exhaust fan. Wait at least 30 minutes.

5.1.17.2 Turn on the chiller set to 20° C. Wait at least one hour.

5.1.18 Start the analysis using the method for glass.

- Open ESI and iTEVA software.
- Turn on plasma.

- Initialize system through the ESI CI window.
- Open <Analyst> in iTEVA.
- Add glass weights and correction factor.
- Run autosession.

5.1.19 Print a report of the results.

5.2 Instrumental Conditions

This analysis is performed using a Thermo Fischer Scientific iCAP 6500 Duo ICP-OES.

Analysis Preferences:

Sample Options	#Repeats:	3		
	Delay Time:	0.0 seconds		
	Sample Flush Time:	22 seconds		
	Analysis mode:	Speed		
Source	Sample Introduction:	Nebulizer		
	Plasma View:	Radial		
Analysis Maximum	Low WL Range:	Axial 15	Radial 15	
Integration Time (sec)	High WL Range:	Axial 5	Radial 8	
Calibration Mode	Concentration			
Trailing Full Frame	Intelli-Frame:	Yes		
Options	Max Integration Time (sec):	30		
	WL Range:	Low		
	View:	Radial		

Source Settings:

Nebulizer Pump:	Flush Pump Rate (rpm):	38
	Analysis Pump Rate (rpm):	38
	Pump Relaxation Time (sec):	0
	Pump Tubing Type:	Tygon Orange/White
	RF Power:	1150 W
	Nebulizer Flow:	0.57 L/min
	Auxiliary Gas:	0.8 L/min

Analytical Wavelengths:	Al	396.152 (nm)
	Ba	455.403
	Ca	315.887
	Fe	259.837
	Mg	285.213
	Mn	260.569
	Na	818.326
	Sr	407.771
	Ti	338.376
	Zr	343.823
	Sc	361.384

Preferences may be altered at the discretion of the Geologist-Forensic Examiner. Any changes to the analysis conditions must be recorded in the case notes.

5.3 Interpretation of the Analytical Results

5.3.1 Following the recommendations of Trejos et al (2013), a modified 4σ confidence interval is used as the comparison criterion for the comparative analysis of glass fragments by ICP-OES. If the average elemental concentration for any element in the item being compared falls outside of the modified 4σ confidence interval for any element in an exemplar sample, the items are considered distinguishable.

5.3.2 If measured elemental concentrations are between the limit of detection and the limit of quantitation of the instrument, measured concentration values are unreliable and may produce extremely high RSDs. In this case, reanalysis and/or re-preparation of the samples is not useful. While it is possible to report the presence of an element if the concentration of the element is between the limit of detection and the limit of quantitation, the concentration will not be reported.

5.3.3 The detection limits of this method vary slightly from day to day. Approximate method detection limits have been stated in the validation records for the Thermo Fischer Scientific iCAP 6500 Duo ICP-OES. These values may be used as a guide, but a better approximation can be determined for each particular case when needed.

6 Calculations

A modified 4σ confidence interval is calculated by taking either the measured standard deviation or 3% of the average for each element, whichever is greater, and multiplying it by four. The confidence interval for an element is the average value of the elemental concentration \pm the modified 4σ .

7 Measurement Uncertainty

Not applicable.

8 Limitations

8.1 RSDs may be unacceptably high in specimens containing less than 3 mg of glass.

8.2 Analysis of glass using ICP-OES is destructive. ICP analysis will not be possible if it is necessary to preserve all of the glass.

9 Safety

9.1 Glass digest solutions are classified as hazardous materials and must be handled and disposed of in accordance with procedures set forth in the FBI Laboratory Safety Manual.

9.2 Personal protective equipment (PPE) must be worn when handling mineral acids, particularly hydrofluoric acid (HF), including gloves, safety glasses, and a laboratory coat. HF is corrosive to all body tissues and bone. Extreme care must be exercised in the presence of this acid. Prior to first use, all personnel handling HF must complete HF Training and successfully pass the HF Quiz provided by the Health, Safety, and Security Unit. While handling HF, a second person who has completed and passed HF training must be present.

9.3 Outside venting of exhaust gases from the ICP instrument and from the oven used for removal of silicon fluorides during glass specimen dissolution is maintained.

9.4 Breaking glass can cause glass fragments to be ejected in unpredictable trajectories. Use caution to break the glass in a way that minimizes blowback. Broken glass can cause cuts and damage to eyes and exposed skin. PPE must be worn when handling or breaking glass including gloves, safety glasses, and a laboratory coat.

10 References

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- Spectroscopy With a Hydrofluoric Acid Resistant Torch, *Journal of Analytical Spectrometry*, Volume 4, February 1989.
- FBI Laboratory Safety Manual (current version)
- Thermo Fisher Scientific iCAP 6500 Duo ICP-OES Operation Manual.

Rev. #	Issue Date	History
3	02/10/2020	<p>Section 4.1 changed “item” to “source.”</p> <p>Changed Sections 5.1.4 and 5.1.8 to active voice.</p> <p>Changed 5.3.1 to conform to other TEU documents.</p> <p>Added sections 3.1.3, 3.3, and 3.5 and renumbered following sections as necessary.</p> <p>Changed “the glass digestion” to “a calibration” in sections 3.1 and 3.1.4.</p> <p>Changed “may” in section 4.3 to “must.”</p> <p>Requirement to use a weight sheet removed from section 5.1.8.</p> <p>Grammar corrected in 5.1.11.</p> <p>Updated the Health, Safety, and Security Unit name in section 9.2.</p>
4	09/01/2021	<p>Added reference to Section 1.2.</p> <p>Formatting corrected in Section 3.</p> <p>Updated Section 3.2.1.2 for clarity.</p> <p>Changed “Mineralogy” to “Geology” in Approval Section.</p> <p>Changed TL in Approval Section.</p>

Approval

Redact - Signatures on File

Trace Evidence Unit Chief _

Date: 08/31/2021

Geology Technical Leader _

Date: 08/31/2021